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ORDERING AND PLASTIC DEFORMATION IN ZIRCONIA BASED  
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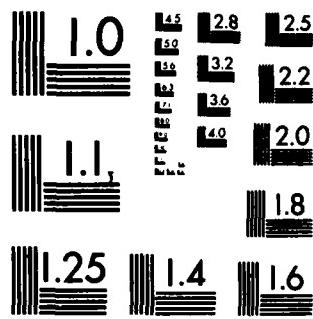
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ORDERING AND PLASTIC DEFORMATION IN ZIRCONIA-BASED CERAMICS

Final Report

T. E. Mitchell and A. H. Heuer

May 1983

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Department of Metallurgy and Materials Science  
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Cleveland, Ohio 44106

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Various aspects of phase transformations and deformation of $ZrO_2$ -CaO and $ZrO_2-Y_2O_3$ ceramics have been studied. The kinetics of precipitation of both tetragonal ( $t-ZrO_2$ ) and $CaZr_4O_9$ ( $\phi_1$ ) from cubic $ZrO_2$ -CaO solid solutions have been studied. The precipitation and growth of the precipitates proceed by nucleation and growth and quantitative analysis shows good agreement with data		

on diffusion rates and interfacial energies.  $\Phi_1$  is found to be metastable with respect to  $\Phi_2$ -Ca<sub>6</sub>Zr<sub>19</sub>O<sub>44</sub> after aging.  $\Phi_2$  has much higher coherency strains than  $\Phi_1$ .

Plastic deformation of single crystals of  $ZrO_2$ -CaO has been studied at high temperatures. The primary slip system is  $\{001\} <110>$  and the secondary system is  $\{1\bar{1}\bar{1}\} <110>$ . Both hypo- and hypereutectoid compositions showed precipitation hardening when aged. Dislocation substructures have been examined by transmission electron microscopy and observations include channels devoid of precipitates which are induced to dissolve by dislocation motion.

$\text{ZrO}_2\text{-Y}_2\text{O}_3$  has also been studied for comparison. Single crystals are found to be almost 100% tetragonal; this metastable t' phase has a higher  $\text{Y}_2\text{O}_3$  content than the normal t phase and is believed to form by a massive transformation from the cubic phase. Annealing causes the t' to decompose into colonies of two t variants plus cubic.



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Statement of Problem

Zirconia-based ceramics are finding increasing applications in diverse areas where high toughness is required. The present research program was undertaken to investigate some poorly understood aspects of their structure. One area was the structure of the cubic solid solution and its decomposition into tetragonal and ordered phases. The other was the deformation behavior and the nature of dislocations in zirconia.

Summary of Results

(a) Precipitation in Ca-Stabilized Zirconia.

The initial phase of this work is best described in terms of the Abstract of the Ph.D. Thesis of J. M. Marder.

The kinetics of precipitation of both tetragonal zirconia ( $ZrO_2$ ) and  $CaZr_4O_9$  ( $\phi_1$ ) from cubic calcia-stabilized zirconia solid solutions were studied using transmission electron microscopy (TEM). A hypo-eutectoid (8.5 mole % CaO) hot-pressed polycrystal was used to investigate precipitation of tetragonal zirconia, and a hyper-eutectoid (16 mole % CaO) single crystal was used to investigate precipitation of  $\phi_1$ . The hypo-eutectoid material could not be quenched rapidly enough from the solution treatment temperature to retain the cubic solid solution; 1-2 nm particles of tetragonal  $ZrO_2$  were present in quenched samples. Therefore, the precipitation of tetragonal particles could not be characterized from the nucleation stage. The coarsening of tetragonal particles proceeded by diffusional growth following the Greenwood-Lifshitz-Slyozov-Wagner (GLSW) theory, with an apparent activation energy of 425 kJ/mole, close to the activation energy for diffusion of calcium and zirconium in calcia-stabilized zirconia. The interfacial energy between the cubic solid solution and the tetragonal precipitates was estimated from the GLSW theory as  $0.5 \text{ J/m}^2$ .

Fine particles generally retained tetragonal symmetry upon cooling to room temperature. However, after extended annealing treatments at 1300°C and 1400°C, some of the coarse particles transformed to either monoclinic zirconia, or to a new phase, designated zeta ( $\zeta$ ). Zeta phase may arise as a result of strain-induced transformation during specimen preparation, or may possibly be a transformation product that developed during cooling from the annealing temperature.

The precipitation and growth of  $\phi_1$  proceeded by nucleation and diffusional growth, and an isothermal transformation (IT) diagram showing the time required for initiation of the reaction as a function of annealing temperature was constructed. The activation energy for  $\phi_1$  coarsening was estimated from the GLSW theory to be 390 kJ/mole, essentially the same as that for the coarsening of tetragonal zirconia precipitates and also corresponding to the diffusion of calcium and zirconium. The interfacial energy between the cubic solid solution and  $\phi_1$  was approximately  $0.2 \text{ J/m}^2$ . The space group of  $\phi_1$  was determined through the use of convergent beam electron diffraction (CBD) to be C2/c, identical to  $\text{CaHf}_4\text{O}_9$ .

Prominent diffuse scattering originated from the cubic solid solution in both hypo- and hyper-eutectoid materials. In hyper-eutectoid material, the diffuse intensity sharpened into discrete  $\phi_1$  reflections but was still present in hypo-eutectoid material after precipitation of tetragonal  $\text{ZrO}_2$ . The origin of diffuse scattering in the latter case is not fully understood.

This work was followed by studying the stability of the  $\phi_1$  phase in CSZ single crystals containing 16-20 mol % CaO. Heat treatment at 1200°C and subsequent analysis by TEM has shown that the  $\phi_1\text{-CaZr}_4\text{O}_9$  is metastable and is gradually replaced by  $\phi_2\text{-Ca}_6\text{Zr}_{19}\text{O}_{44}$ . There are two factors involved in explaining

why  $\phi_1$  forms first: it has a lower CaO content and it has a lower coherency strain with the cubic matrix.

The latest diagram due to Stubican and Hellman (Mat. Res. Bull. 17, 459, 1982) is shown in Fig. 1. Our findings show that in specimens of 17-19 m/o CaO,  $\phi_1$  transforms to  $\phi_2$  within 50-100 hours of annealing at 1200°C is in clear disagreement with the predictions of Fig. 1. Diffraction patterns illustrating the transformation are shown in Fig. 2. The strain contrast from  $\phi_2$  precipitates is illustrated in Fig. 3, which also shows alignment along <100> due to elastic interactions. Details are given in the preprint in Appendix 1.

(b) Phase Stability in  $ZrO_2-Y_2O_3$

$Y_2O_3$  stabilizes the cubic phase field of  $ZrO_2$  as do CaO and MgO. However, there are some interesting differences. We have discovered that single crystals of 6-8 w/o  $Y_2O_3$  material are almost 100% tetragonal. Microstructural and microchemical analysis using analytical electron microscopy has shown that this tetragonal phase (which we call t') has a high  $Y_2O_3$  content and is metastable. Annealing causes the t' to transform into the low  $Y_2O_3$  tetragonal phase (t) plus cubic. The t phase occurs in the form of colonies of two tetragonal variants separated by low energy coherent twin boundaries. We postulate that the t' phase forms directly from the high temperature cubic phase by a massive transformation.

(c) Plastic Deformation of Calcia Stabilized Zirconia

The earlier stages of this research are summarized in the Abstract of the M.S. Thesis of C. E. Voegele.

Single crystals of hypereutectoid CSZ were deformed between 1300°C and 1800°C along [123], [001], and [133] compression axes in order to study primary, secondary, and duplex slip. Using slip trace analysis techniques, the primary {001}<110> system was confirmed, and the secondary slip system was determined to be {111}<110>. Little plastic anisotropy was found between the systems. Long

glide dislocations were observed at small strains, while uniform tangles of climbing dislocations were seen at large strains.

Single crystals of hypoeutectoid CSZ, aged prior to deformation to produce tetragonal precipitates, were considerably stronger than their unaged counterparts. Single crystals of hypereutectoid CSZ, containing  $\text{CaZr}_4\text{O}_9$  precipitates prior to deformation, were also studied and found to be stronger than their unaged counterparts. The precipitates and dislocations in both the hypo- and hypereutectoid crystals were imaged; however, more work must be done in this area in order to fully characterize the precipitate-dislocation interactions.

Further studies of precipitation hardening due to tetragonal in hypoeutectoid and  $\phi_1$  in hypereutectoid have been undertaken. Fig. 4 shows stress strain curves that demonstrate the existence of strong precipitation hardening in hypereutectoid material. TEM was performed on foils cut parallel to the (001) slip plane. Fig. 5 shows that dislocations are concentrated in channels surrounded by precipitates which exhibit a high strain contrast. The channels are free of precipitates, implying that the precipitates are sheared by the dislocations and subsequently dissolve. Fig. 6 shows a series of micrographs taken under different imaging conditions where there are precipitates in the lower left and dislocations and relatively few precipitates in the upper right. Fig. 6(a) is a WBDF picture showing both precipitates and dislocations. Fig. 6(b) is a DF picture showing precipitates only. Fig. 6(c) is a BF picture showing the matrix strain contrast. Fig. 6(d) is a WBDF picture showing dislocations in the matrix. This is the first observation of dislocation channeling in a ceramic system although it has been observed previously in some metallic alloys and irradiated metals. In conclusion, this research has been highly successful and accomplished essentially all that was proposed. Two students obtained theses from the research and a good start was made by two others. Fortunately they were able to transfer two reasonably well-related projects and so this important research area will continue to be investigated.

Publications

J. M. Marder, T. E. Mitchell and A. H. Heuer, "Precipitation From Cubic ZrO<sub>2</sub> Solid Solutions", *Acta Met.* 31, 387 (1983).

J. M. Marder, A. H. Heuer and T. E. Mitchell, "Kinetics of Precipitation in Calcia Stabilized Zirconia", *Phase Transformation*, H. I. Aaronson, ed., p. 727 (1983).

J. W. Hangas, T. E. Mitchell and A. H. Heuer, "Precipitation of  $\phi_1$ -CaZr<sub>4.99</sub>O<sub>9.99</sub> and  $\phi_2$ -Ca<sub>6</sub>Zr<sub>19</sub>O<sub>44</sub> in Calcia-Stabilized Zirconia", *Electron Microscopy Soc. of Amer. Proceedings*, in press (1983).

An additional publication is being prepared for the Zirconia Conference in Stuttgart (May 1983) and the work on plastic deformation is also in preparation.

Participating Scientific Personnel

1. J. M. Marder, Ph.D. (1982).
2. C. E. Voegele, M.S. (1982).
3. V. Lanteri, did not finish Ph.D. while being supported on the Army Contract but will complete thesis on ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> in 1984.
4. J. W. Hangas, did not finish M.S. while being supported on the Army Contract but will complete thesis on plastic deformation in 1983.

APPENDIX 1. From Proceedings of the Electron Microscopy Society of America,  
G. W. Bailey, ed., Claitor's, in press (1983).

PRECIPITATION OF  $\phi_1$ -CaZr<sub>4</sub>O<sub>99</sub> and  $\phi_2$ -Ca<sub>6</sub>Zr<sub>19</sub>O<sub>44</sub> IN CALCIA-STABILIZED ZIRCONIA

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INTRODUCTION. CaO stabilizes the high temperature cubic phase field of ZrO<sub>2</sub> resulting in an eutectoid reaction at 1140°C, as shown in Fig. 1 [1]. Two ordered defect structures are known to occur in the zirconia-calcia system on the hypereutectoid side of the cubic phase field. One is a monoclinic precipitate called  $\phi_1$ , with the composition of CaZr<sub>4</sub>O<sub>9</sub>, whereas the other is a rhombohedral precipitates (R3c) called  $\phi_2$  which has a composition of Ca<sub>6</sub>Zr<sub>19</sub>O<sub>44</sub>[1]. The names of the precipitates are derived from analogous structures in the calcia-hafnia system, and these structures are described by Allpress, et al. [2]. The present study has been designed to use TEM to describe the microstructures more fully.

EXPERIMENTAL. Single crystals of calcia-stabilized zirconia (CSZ) of 16-20m/o were heat treated in air from 20-100 hr at 1200°C. Foils were prepared by ion-thinning, and their composition and microstructure were analyzed on a Phillips EM400T analytical electron microscope.

RESULTS. Fig. 2a is a [110] zone axis diffraction pattern of a 17m/o specimen aged for 20 hr at 1200°C which shows both  $\phi_1$  and  $\phi_2$  precipitate reflections. Fig. 2b is a diffraction pattern of the same zone axis in another specimen of the same composition aged for 100 hr at 1200°C which shows only  $\phi_2$  reflections; all the  $\phi_1$  has transformed to  $\phi_2$ . This shows that  $\phi_1$  is metastable in the composition range of 17m/o, whereas the phase diagram prepared by the reactive gel process in Fig. 1 predicts that it should be stable.

The  $\phi_1$  precipitates in Fig. 3a are approximately 90-130nm long after being aged for 336 hr at 1200°C in a crystal of 16m/o CSZ [3]. The precipitates are equiaxed, and mostly randomly distributed, although they do form some random clusters. The  $\phi_2$  precipitates in Fig. 3b were grown for 100 hr at 1200°C in 17m/o CSZ. They are 25 nm wide and tend to align themselves along <100><sub>c</sub> directions to relieve the high coherency strains which cause high strain contrast in bright field. The  $\phi_1$  precipitates exhibit less strain contrast and have less tendency to align themselves along <100><sub>c</sub> directions. Both Figures 3a and 3b were taken near a <100><sub>c</sub> zone axis.

DISCUSSION. The existence of the  $\phi_1$  and  $\phi_2$  phases is not completely understood. However, the present results show that  $\phi_1$  may be a metastable phase due to the high coherency strains that could make  $\phi_2$  to nucleate, as well as the fact that it contains more calcia than  $\phi_1$ . This work has shown the usefulness of TEM in studying single crystals to serve as a check on phase diagrams prepared using finer grained processes.

REFERENCES

1. J.R.Hellmann and V.S.Stubican, Mat. Res. Bull., 17, 459 (1982).
2. J.G.Allpress, et al., J. Solid State Chem., 14, 264 (1975).
3. Specimen from J.M.Marder, T.E.Mitchell and A.H.Heuer, Acta Met., 31, 387 (1983). This work was supported by the Army Research Office.

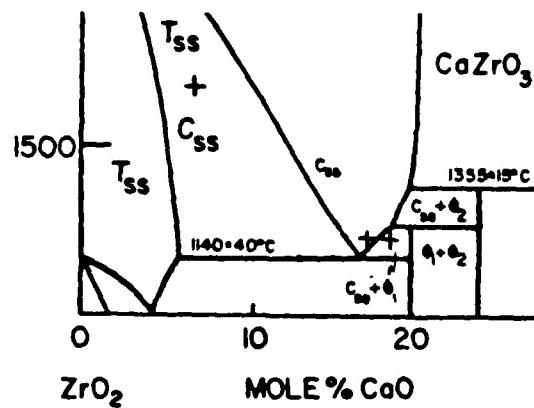


Fig. 1. Zirconia-calcia phase diagram [1]. Specimen composition in this study are marked with crosses.

Fig. 2. <110> diffraction patterns from 17m/o crystals: (a) aged 20 hr showing both  $\phi_1$  and  $\phi_2$  reflections in the fcc matrix, the former being stronger than the latter; (b) aged for 100 hr showing only  $\phi_2$  reflections, the metastable  $\phi_1$  having transformed to  $\phi_2$ .

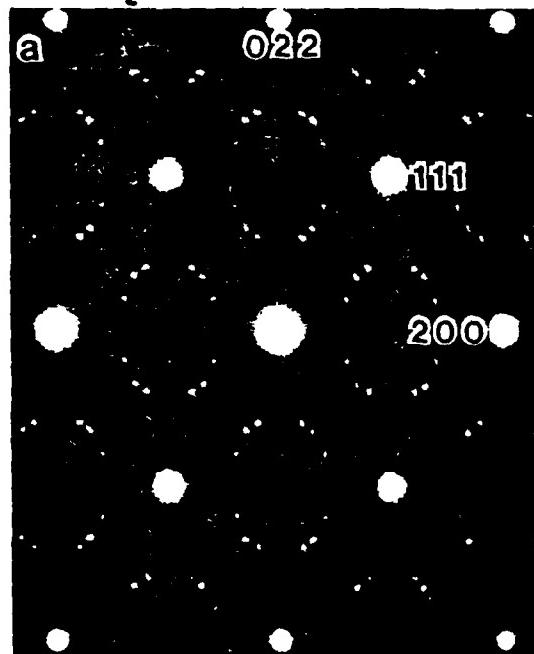


Fig. 3a. DF of  $\phi_1$  precipitate in 16m/o CSZ aged for 336 hr at 1200°C.

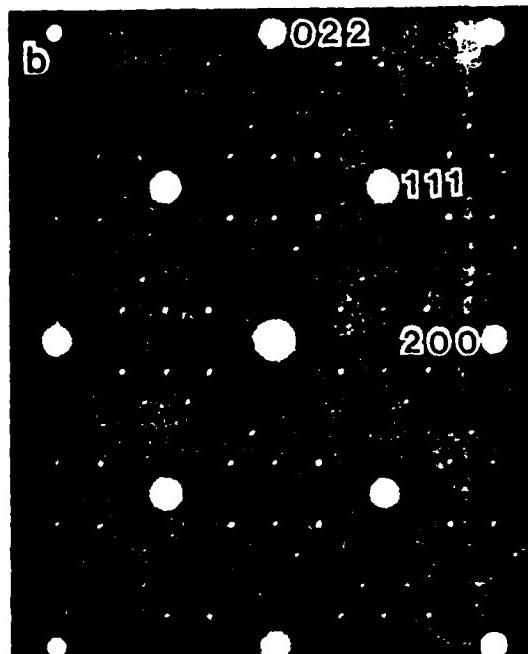


Fig. 3b. DF of  $\phi_2$  precipitate in 17m/o CSZ aged for 100 hr at 1200°C. Note the tendency to align along [001].

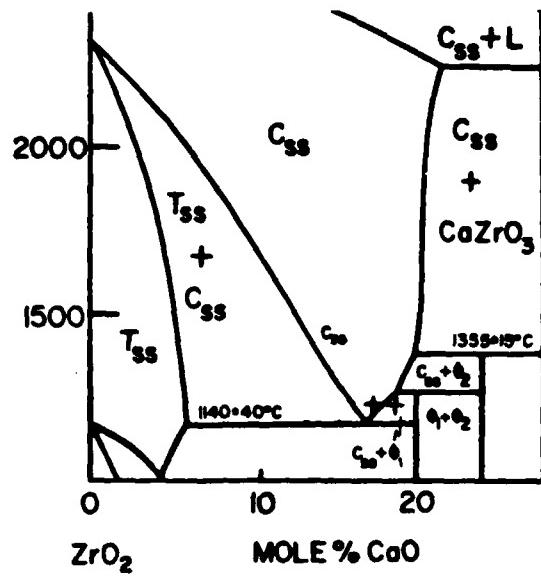


Fig. 1.  $\text{ZrO}_2$  rich portion of the  $\text{ZrO}_2$ - $\text{CaO}$  phase diagram, from Stubican and Hellman.

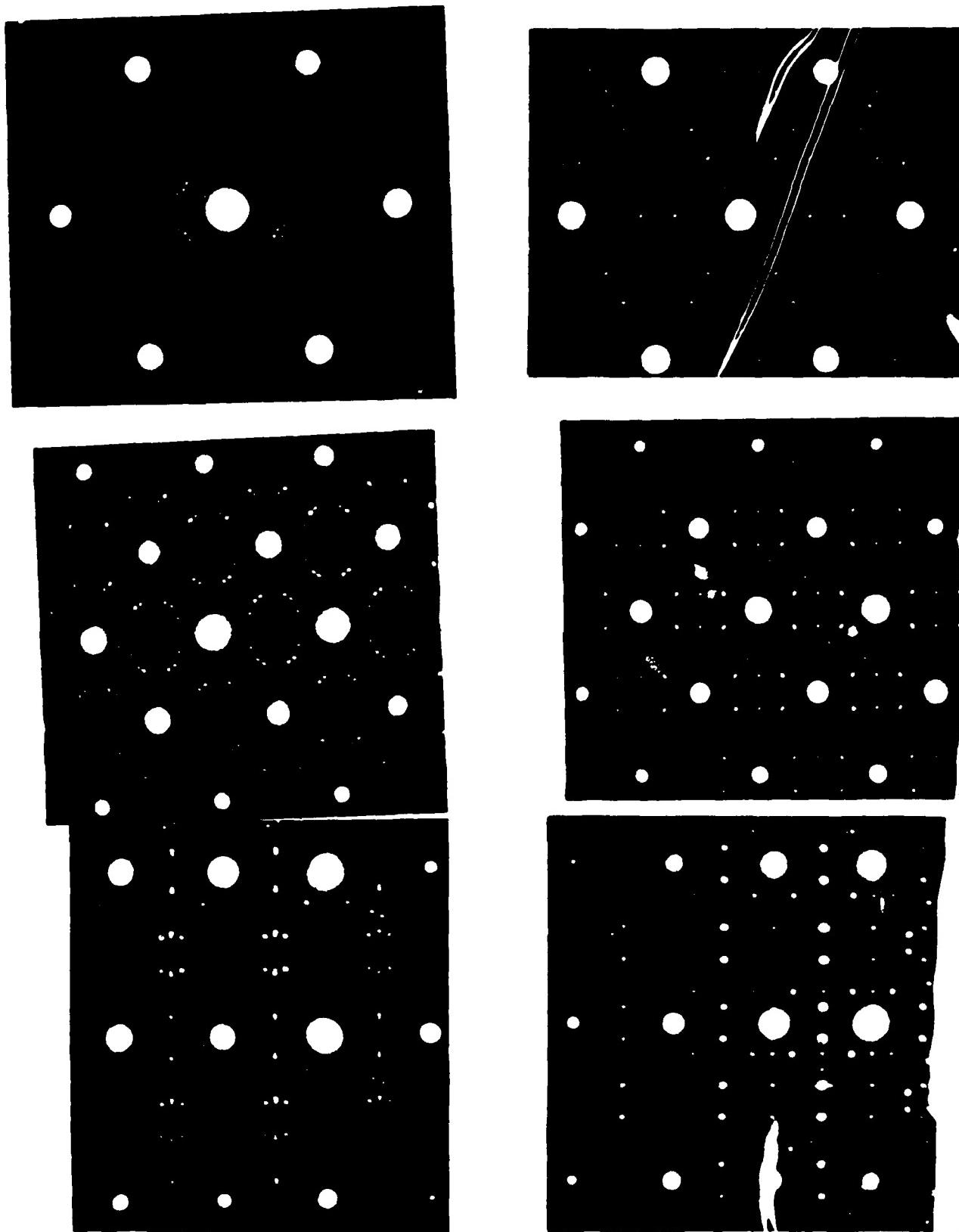
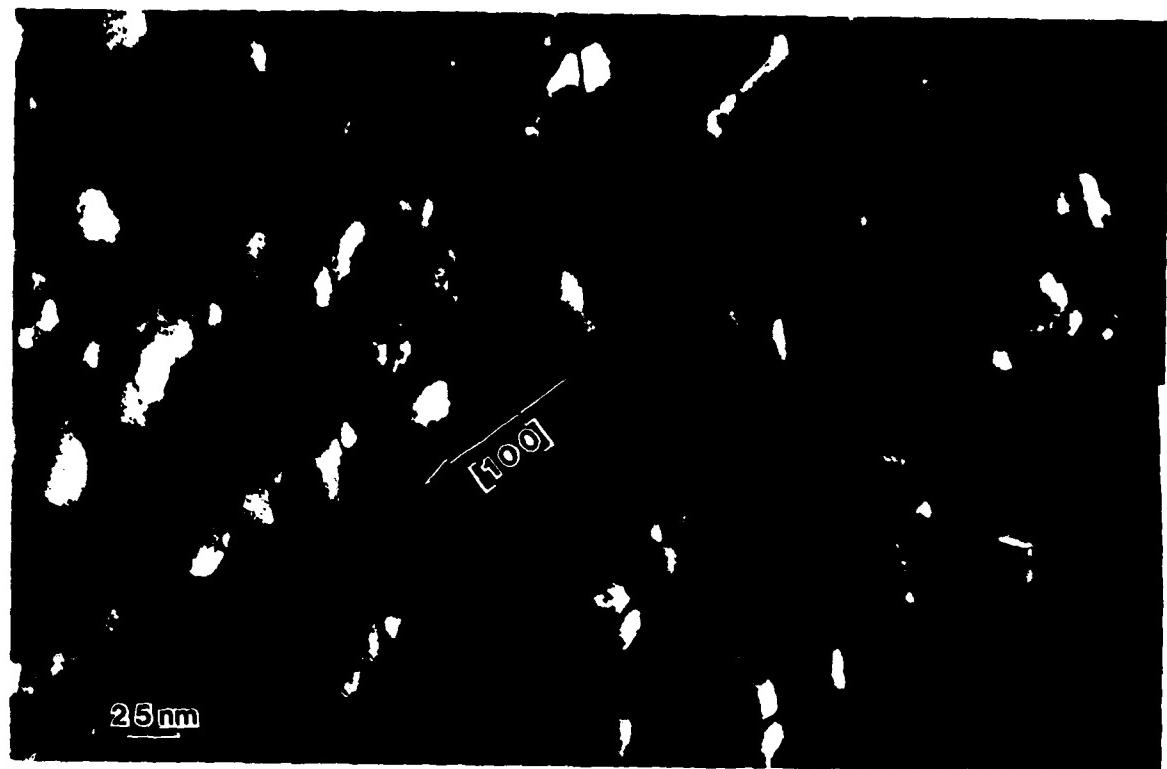


Fig. 2. Diffraction patterns from  $ZrO_2$ -17m/o  $CaO_9$ : left (aged 20 hrs at  $1200^\circ C$ ) mostly  $\phi_1$ ; right (aged 100 hrs) only  $\phi_2$ . Top to bottom are [111], [110] and [112] zones respectively.



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Fig. 3.  $\phi_2$  precipitates imaged in DF showing strong tendency to align along  $<100>$ .

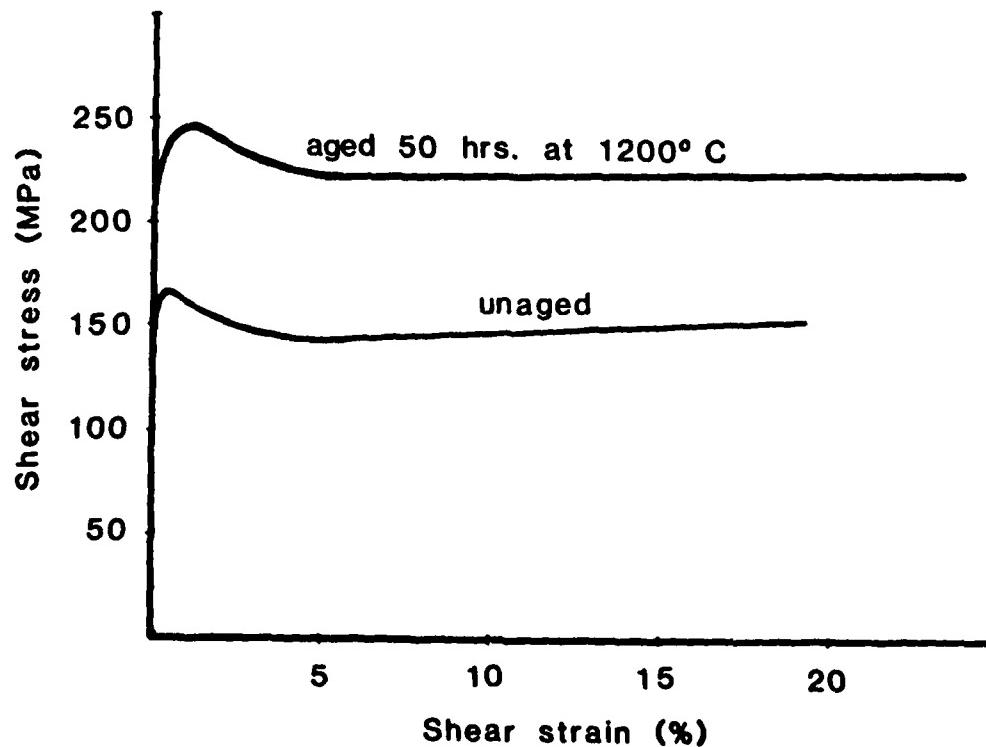


Fig. 4. Stress-strain curves of unaged (cubic) and aged (cubic +  $\phi$  precipitates) hypereutectoid crystals showing strong precipitation hardening.



Fig. 5. Precipitate-free channel containing dislocations in aged and deformed hyperstoichiometric crystal.

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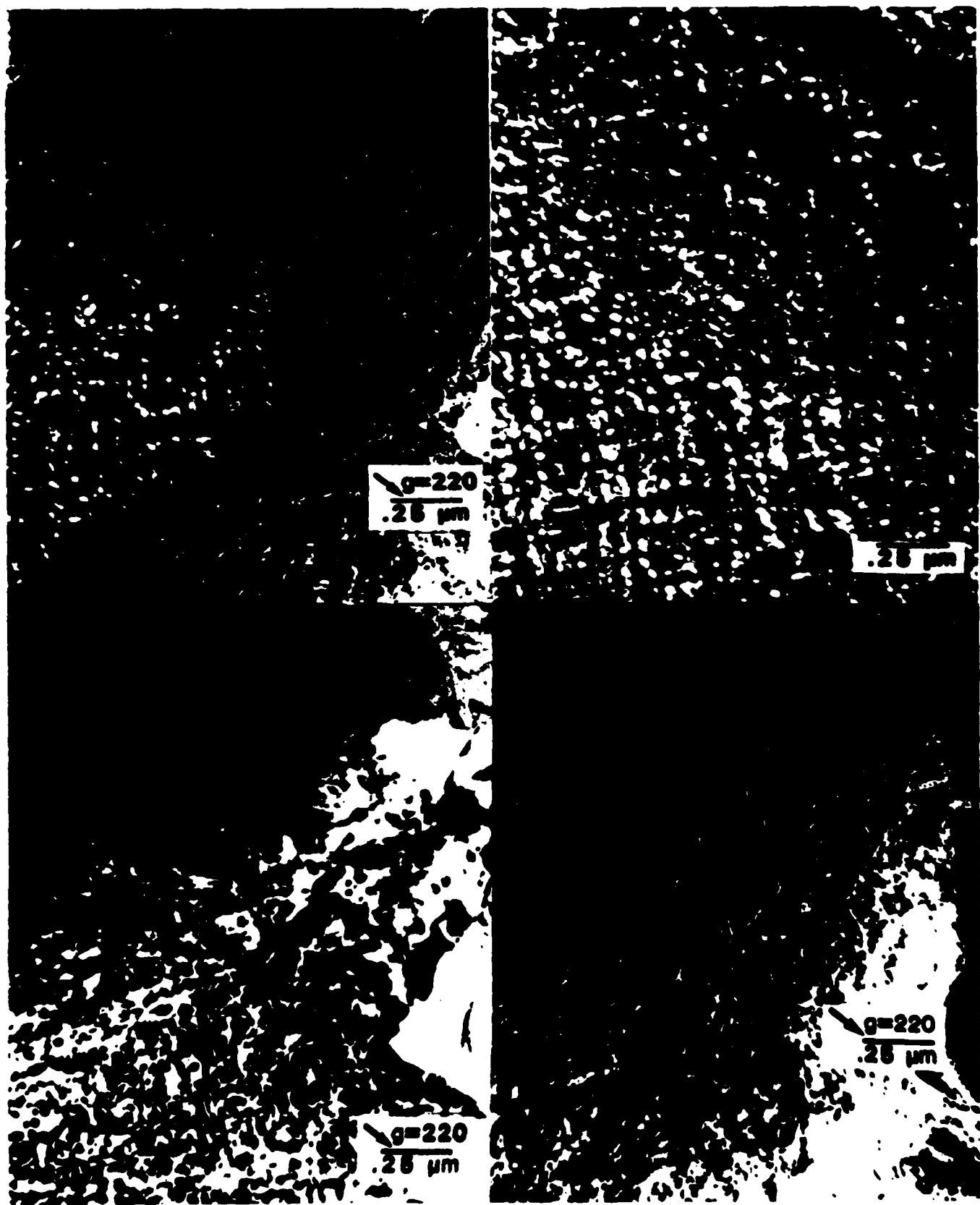


Fig. 6. Aged and deformed hyperstoichiometric crystal: (a) WBDF of  $\phi$  and dislocations, (b) DF of  $\phi$  only, (c) BF of matrix strain contrast, (d) WBDF of dislocations only.

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